

(19)



Europäisches Patentamt  
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(11) Publication number:

**0 283 164 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

- (45) Date of publication of patent specification: **24.05.95** (51) Int. Cl.<sup>6</sup>: **C08F 210/00, C08F 232/00,**  
**/(C08F210/00,232:00),**  
**(C08F232/00,210:00)**
- (21) Application number: **88301791.5**
- (22) Date of filing: **01.03.88**

The file contains technical information submitted  
after the application was filed and not included in  
this specification

- (54) **Cyclo-olefinic random copolymer, olefinic random copolymer, and process for producing cyclo-olefinic random copolymers.**

- (30) Priority: **02.03.87 JP 45152/87**  
**11.12.87 JP 312112/87**  
**15.12.87 JP 315206/87**  
**01.02.88 JP 19622/88**

- (43) Date of publication of application:  
**21.09.88 Bulletin 88/38**

- (45) Publication of the grant of the patent:  
**24.05.95 Bulletin 95/21**

- (84) Designated Contracting States:  
**DE FR GB IT NL**

- (56) References cited:  
**EP-A- 0 129 368 EP-A- 0 156 464**  
**EP-A- 0 185 918 EP-A- 0 203 799**  
**DE-A- 1 570 910 US-A- 3 725 366**

- (73) Proprietor: **MITSUI PETROCHEMICAL INDUSTRIES, LTD.**  
**2-5, Kasumigaseki 3-chome**  
**Chiyoda-ku**  
**Tokyo 100 (JP)**

- (72) Inventor: **Ishimaru, Naoshi**

**4-9, Waki 2-chome**  
**Waki-cho**  
**Kuga-gun**  
**Yamaguchi-ken (JP)**  
Inventor: **Tsutsui, Toshiyuki**  
**3-6, Misono 1-chome**  
**Ohtake-shi**  
**Hiroshima-ken (JP)**  
Inventor: **Toyota, Akinori**  
**103-21, Minami-iwakuni-cho 2-chome**  
**Iwakuni-shi**  
**Yamaguchi-ken (JP)**  
Inventor: **Kashiwa, Norio**  
**18-22, Yamate-cho 1-chome**  
**Iwakuni-shi**  
**Yamaguchi-ken (JP)**

- (74) Representative: **Myerscough, Phillip Boyd et al**  
**J.A.KEMP & CO.**  
**14, South Square**  
**Gray's Inn**  
**London WC1R 5LX (GB)**

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## Description

This invention relates to a novel cyclo-olefinic random copolymer, in particular to the provision of a cyclo-olefinic random copolymer having excellent transparency, thermal stability, heat aging resistance, chemical resistance, solvent resistance, dielectric properties and mechanical properties and a narrow molecular weight distribution and a narrow composition distribution.

This invention further relates to a process for producing a cyclo-olefinic random copolymer by copolymerizing an alpha-olefin, a cyclo-olefin and optionally a cyclic polyene, in the presence of a highly active polymerization catalyst, formed from a transition metal compound and an aluminoxane.

Known processes for producing cyclo-olefinic copolymers by copolymerizing alpha-olefins such as ethylene and cyclo-olefins involve the use of titanium-containing catalysts comprising titanium compounds and organoaluminum compounds or vanadium-containing catalysts comprising vanadium compounds and organoaluminum compounds.

In a copolymerization process using a titanium-containing catalyst, a cyclo-olefin has lower reactivity than an alpha-olefin such as ethylene and the copolymerization efficiency is low. In order, therefore, to expect production of a copolymer of the cyclo-olefin with the alpha-olefin, it is necessary to add the cyclo-olefin in a large quantity to the polymerization system. The presence of a large quantity of the cyclo-olefin reduces the activity of the catalyst and may result in a decrease in the molecular weight of the resulting copolymer. It is difficult therefore to obtain a high-molecular-weight copolymer. Moreover, this process has the defect that side-reactions such as the ring-opening polymerization of the cyclo-olefin tend to occur, and the resulting polymer has a broad molecular weight distribution. On the other hand, in a copolymerization process using a vanadium-containing catalyst, the copolymerization efficiency of the cyclo-olefin is higher than in the case of using the titanium-containing catalyst and the resulting copolymer has a narrow molecular weight distribution. But it has the defect that the polymerization activity is generally very low.

Catalysts comprising transition metal compounds and aluminoxanes are proposed as highly active polymerisation catalysts for olefins in, for example, JP-A-19309/1983, 95292/1984, 35005/1985, 35006/1985, 35007/1985 and 35008/1985. Of these, JP-A-19309/1983, 35005/1985, 35006/1985, 35007/1985 and 35008/1985 describe that these catalyst systems can be applied to the copolymerization of ethylene with other alpha-olefins. With regard to the production of cyclo-olefinic copolymers, JP-A-221206/1986 discloses a catalyst comprising a transition metal compound and an aluminoxane with regard to the production of a copolymer of an alpha-olefin and a cyclo-olefin. This catalyst, however, has low polymerization activity, and is difficult to obtain the copolymer in good yields.

It is generally known that by using Ziegler-type catalysts comprising a combination of titanium or vanadium compounds and organoaluminum compounds, binary copolymers of ethylene with cyclo-olefins or ternary copolymers of ethylene, alpha-olefins such as propylene or 1-butene and cyclo-olefins are obtained. However, no example has been known in which an alpha-olefin having 3 to 20 carbon atoms was copolymerized with a cyclo-olefin in the absence of ethylene with a Ziegler-type catalyst. Naturally, no such copolymer has been reported so far.

Polycarbonate, poly(methyl methacrylate) and polyethylene terephthalate have been known as synthetic resins having excellent transparency. For example, polycarbonate is a resin having excellent thermal stability, heat aging resistance and impact strength in addition to excellent transparency, but have the disadvantage of being inferior in chemical resistance and susceptible to attack by strong alkalis. Poly(methyl methacrylate) is susceptible to attack by ethyl acetate, acetone and toluene, is swollen in ether and has low thermal stability. Polyethylene terephthalate has excellent thermal stability and mechanical properties, but is susceptible to attack by strong acids or alkalis and liable to undergo hydrolysis.

Many polyolefins widely used as general-purpose resins have excellent chemical resistance, solvent resistance and mechanical properties, but poor thermal stability. Moreover, they have poor transparency because of their crystalline nature. Generally, the transparency of polyolefins is improved by adding a nucleating agent and thereby finely dividing their crystalline structure, or by quenching them to stop growth of crystals. The effects of such techniques, however, have not proved to be entirely satisfactory. Rather, the addition of a third component such as a nucleating agent is likely to reduce the inherent excellent properties of the polyolefins. The quenching method requires a large-sized apparatus, and with a reduction in crystallinity, the polyolefins are likely to be degraded in thermal stability and rigidity.

EP-A-203799 discloses a random copolymer comprising polymerised ethylene units and polymerised cyclo-olefin units which are incorporated into the polymer without ring opening. The mole ratio of cyclo-olefin units to ethylene units is 3:97 to 60:40 and other monomers may be grafted onto the polymer. The catalyst used according to EP-A-203799 is formed from a soluble vanadium compound and an aluminium compound.

EP-A-156464 discloses a random copolymer comprising 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalate, ethylene and optionally an  $\alpha$ -olefin having at least three carbon atoms. The copolymer is prepared by copolymerising the components in the presence of a catalyst formed from a vanadium compound and an organoaluminum compound.

With regard to the copolymerization of ethylene with bulky comonomers, U.S. Patent No. 2,883,372, for example, discloses a copolymer of ethylene and 2,3-dihydrodicyclopentadiene. This copolymer has an excellent balance between rigidity and transparency, but poor thermal stability because its glass transition temperature is about 100 °C. A copolymer of ethylene and 5-ethylidene-2-norbornene has similar defects.

JP-B-14910/1971 proposes a homopolymer of 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydro-naphthalene. This polymer, however, has poor thermal stability and heat aging resistance.

JP-A-127728/1083 proposes a homopolymer of 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene or a copolymer of the above cyclo-olefin and a norbornene-type comonomer. It is clear from this patent document that these copolymers are ring-opened polymers. These ring-opened polymers have poor thermal stability and heat aging resistance because they contain an unsaturated bond in the main polymer chain.

JP-A- Nos. 168708/1985, 98780/1986, 115912/1986, 115916/1986, 120816/1986, 95906/1986 and 95905/1986 disclose that olefinic random copolymers of ethylene and specific bulky cyclo-olefins having a good balance in thermal stability, heat aging resistance, chemical resistance, solvent resistance, dielectric properties and mechanical properties while having transparency, and exhibit excellent performance in the field of optical materials such as optical memory discs and optical fibers. These copolymers contain ethylene copolymerized therein, and in order to impart good thermal stability, a large amount of a cyclo-olefin must be copolymerized. Reaction of such copolymers with maleic anhydride or the like to impart polar property to these copolymers usually requires the use of peroxides. This causes cleavage of the main chain and results in a reduction in molecular weight. It is desired therefore to provide olefinic random copolymers which in spite of a low cyclo-olefin content, have excellent thermal stability and can be modified without using peroxides.

The invention provides a cyclo-olefin random copolymer consisting of units derived from (A) an olefin-olefin component having 3 to 20 carbon atoms, (B) an optional cyclic polyene component, and (C) a cyclo-olefin component,

(i) said copolymer containing at least 5 mole% of recurring units derived from said  $\alpha$ -olefin component and at least 1 mole% of recurring units derived from said cyclo-olefin component, subject to the proviso that when the copolymer is derived also from the cyclic polyene component it contains at least 1 mole% of recurring units derived from said cyclic polyene component and from 2 to 80 mole% of recurring units from said cyclo-olefin component, and

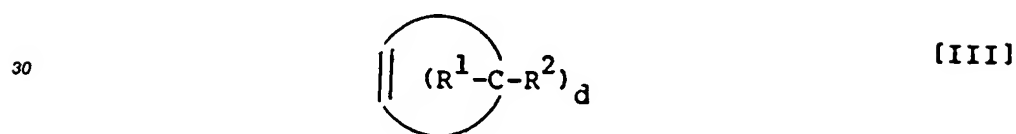
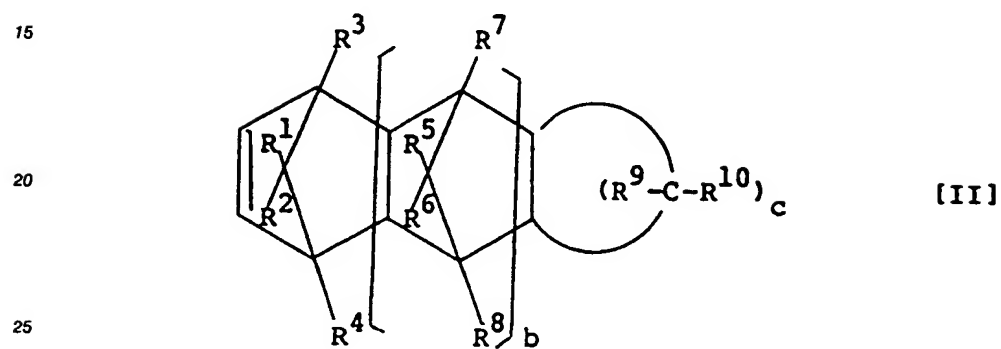
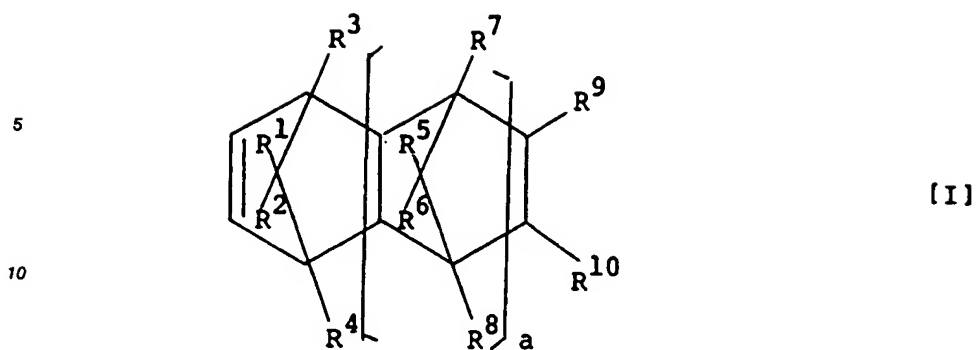
(ii) said copolymer having an intrinsic viscosity  $[\eta]$ , measured in decalin 135 °C, of from 0.01 to 10 dl/g. The invention also provides a process for producing a cyclo-olefinic random copolymer as claimed in any one of the preceding claims, which comprises copolymerizing the  $\alpha$ -olefin, the cyclo-olefin and optionally also the cyclic polyene in the presence of a catalyst formed from

(A) a compound of a transition metal of Group IVB of the periodic table having as a ligand a multi-dentate coordination compound in which at least two conjugated cycloalkadienyl groups or substituted products thereof are bonded via a lower alkylene group, and

(B) an aluminoxane, subject to the proviso that when the cyclic polyene is present the transition metal compound (A) is a zirconium compound containing as ligand at least two indenyl groups or substituted indenyl groups or partially hydrogenated groups thereof which are bonded via an alkylene group.

The cyclo-olefinic random copolymer of this invention is a cyclo-olefinic random copolymer composed of an  $\alpha$ -olefin component having 3 to 20 carbon atoms and a cyclo-olefin component and optionally a cyclic polyene component.

The cyclo-olefin component is a cyclo-olefin represented by the following general formula [I], [II] or [III], and in the cyclo-olefinic random copolymer of this invention, the cyclo-olefin component forms a structure represented by the general formula [IV], [V] or [VI].



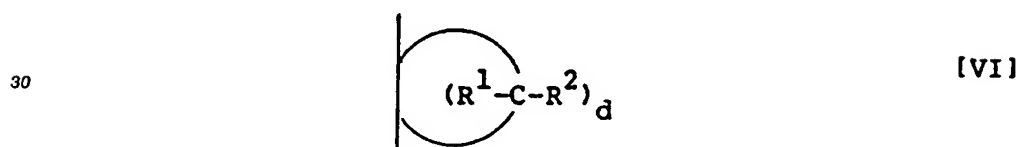
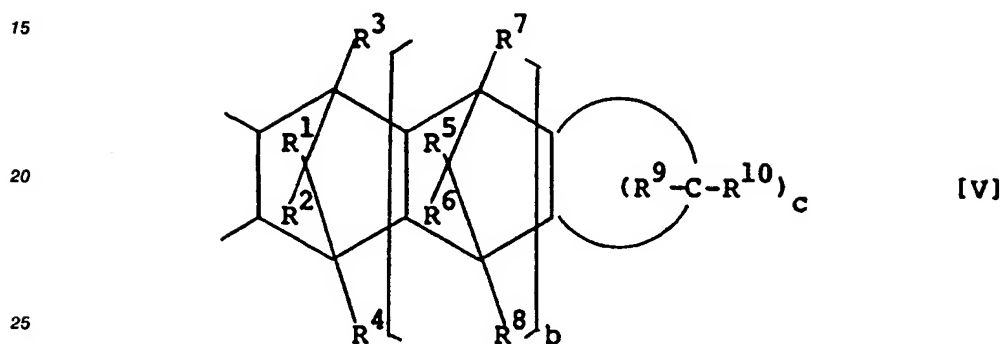
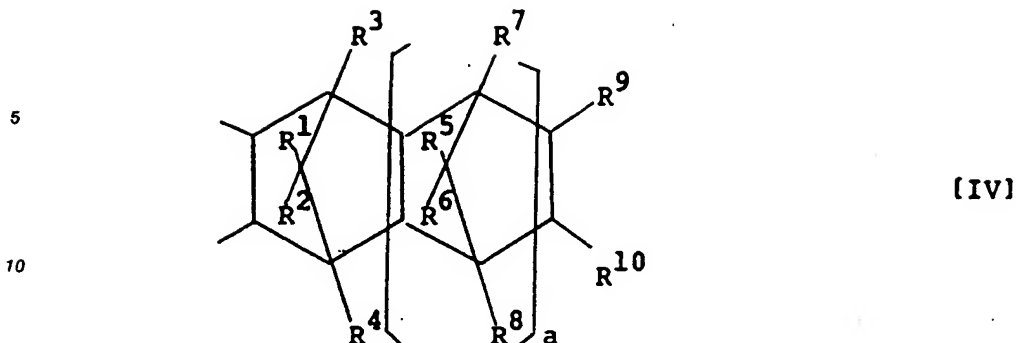
35 In the formulae, a and b are an integer of 0 or more, c and d are an integer of 3 or more, and each of R<sup>1</sup> to R<sup>10</sup> represents a hydrogen atom, a halogen atom or a hydrocarbon group.

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35 In the formulae, a, b, c, d, and R<sup>1</sup> to R<sup>10</sup> are as defined above.

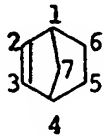

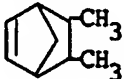

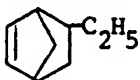
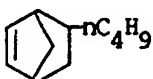
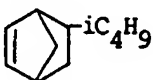
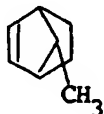
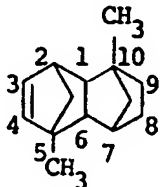
In the production of the cyclo-olefinic random copolymer of this invention, examples of the C<sub>3</sub>-C<sub>20</sub> alpha-olefin used as a material include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene.

40 Cyclo-olefins represented by general formula [I] may be easily produced by condensing cyclopentadienes with the corresponding olefins in accordance with the Diels-Alder reaction. Cyclo-olefins represented by general formula [II] can be easily produced likewise by condensing cyclopentadienes with the corresponding cyclo-olefins in accordance with the Diels-Alder reaction.

Specific examples of the cyclo-olefins of general formula [I] include octahydronaphthalenes such as

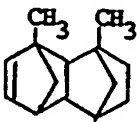
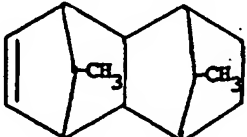
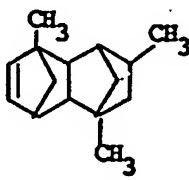
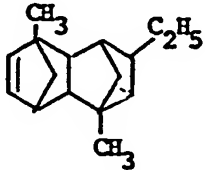
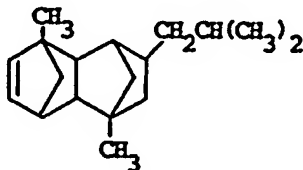
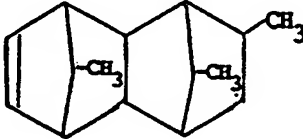
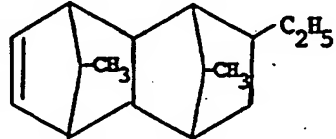
45 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2-propyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2-hexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2-stearyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
50 2,3-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2-methyl-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2-chloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2-bromo-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2,3-dichloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
55 2-cyclohexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
2-n-butyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, and  
2-isobutyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, and;  
the compounds described in Table 1 below.

Table 1

Chemical formula	Chemical name
	bicyclo[2,2,1]hept-2-ene
	6-methylbicyclo[2,2,1]-hept-2-ene
	5,6-dimethylbicyclo[2,2,1]-hept-2-ene
	1-methylbicyclo[2,2,1]-hept-2-ene
	6-ethylbicyclo[2,2,1]-hept-2-ene
	6-n-butylbicyclo[2,2,1]-hept-2-ene
	6-i-butylbicyclo[2,2,1]-hept-2-ene
	7-methylbicyclo[2,2,1]-hept-2-ene
	5,10-dimethyltetracyclo- [4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3-dodecene

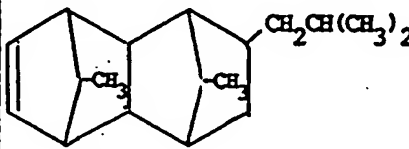
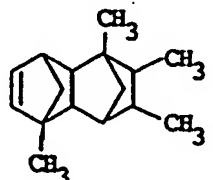
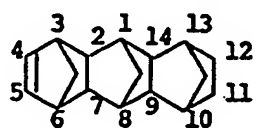
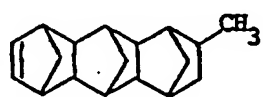
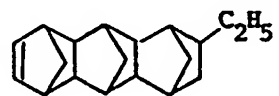
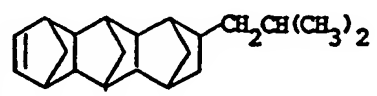
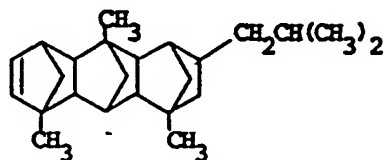
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Table 1 (continued)

Chemical formula	Chemical name
	2,10-dimethyltetracyclo- [4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3-dodecene
	11,12-dimethyltetracyclo- [4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3- dodecene
	2,7,9-trimethyltetracyclo- [4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3-dodecene
	9-ethyl-2,7-dimethyltetra- cyclo[4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3- dodecene
	9-isobutyl-2,7-dimethyltetra- cyclo[4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3- dodecene
	9,11,12-trimethyltetracyclo- [4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3-dodecene
	9-ethyl-11,12-dimethyltetra- cyclo[4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3- dodecene

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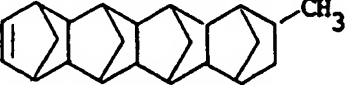
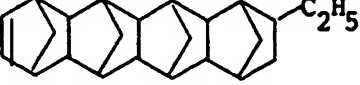
Table 1 (continued)

Chemical formula	Chemical name
	9-isobutyl-11,12-dimethyl-3-tetracyclo[4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3-dodecene
	5,8,9,10-tetramethyltetracyclo[4,4,0,1 <sup>2,5</sup> ,1 <sup>7,10</sup> ]-3-dodecene
	hexacyclo[6,6,1,1 <sup>3,6</sup> ,1 <sup>10,13</sup> ,0 <sup>2,7</sup> ,0 <sup>9,14</sup> ]-4-heptadecene
	12-methylhexacyclo[6,6,1,1 <sup>3,6</sup> ,1 <sup>10,13</sup> ,0 <sup>2,7</sup> ,0 <sup>9,14</sup> ]-4-heptadecene
	12-ethylhexacyclo[6,6,1,1 <sup>3,6</sup> ,1 <sup>10,13</sup> ,0 <sup>2,7</sup> ,0 <sup>9,14</sup> ]-4-heptadecene
	12-isobutylhexacyclo[6,6,1,1 <sup>3,6</sup> ,1 <sup>10,13</sup> ,0 <sup>2,7</sup> ,0 <sup>9,14</sup> ]-4-heptadecene
	1,6,10-trimethyl-12-isobutylhexacyclo[6,6,1,1 <sup>3,6</sup> ,1 <sup>10,13</sup> ,0 <sup>2,7</sup> ,0 <sup>9,14</sup> ]-4-heptadecene

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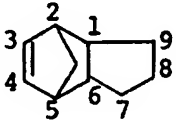
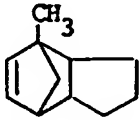
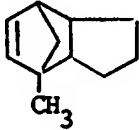
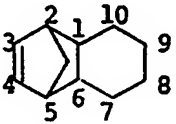
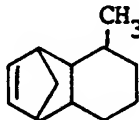
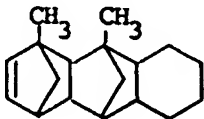
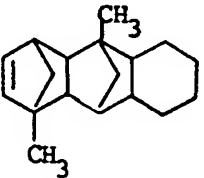


Table 1 (continued)

Chemical formula	Chemical name
	octacyclo-[8,8,1 <sup>2,9</sup> ,1 <sup>4,7</sup> , 1 <sup>11,18</sup> ,1 <sup>13,16</sup> ,0,0 <sup>3,8</sup> ,0 <sup>12,17</sup> ]- 5-dococene
	15-methyloctacyclo-[8,8,1 <sup>2,9</sup> , 1 <sup>4,7</sup> ,1 <sup>11,18</sup> ,1 <sup>13,16</sup> ,0,0 <sup>3,8</sup> , 0 <sup>12,17</sup> ]-5-dococene
	15-ethyloctacyclo-[8,8,1 <sup>2,9</sup> , 1 <sup>4,7</sup> ,1 <sup>11,18</sup> ,1 <sup>13,16</sup> ,0,0 <sup>3,8</sup> , 0 <sup>12,17</sup> ]-5-dococene

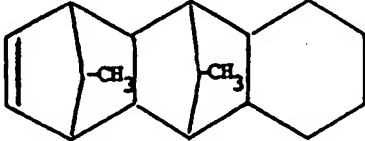
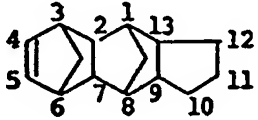
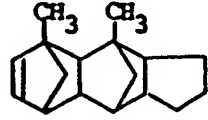
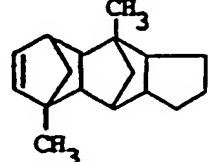
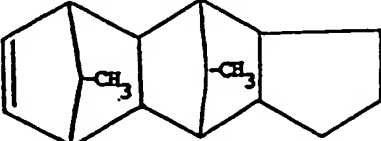
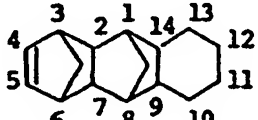
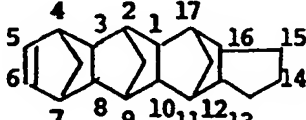
Specific examples of the cyclo-olefins of general formula [II] are compounds shown in Table 2 below.

Table 2

Chemical formula	Chemical name
	tricyclo[4,3,0,1 <sup>2,5</sup> ]-3-decene
	2-methyltricyclo[4,3,0,1 <sup>2,5</sup> ]-3-decene
	5-methyltricyclo[4,3,0,1 <sup>2,5</sup> ]-3-decene
	tricyclo[4,4,0,1 <sup>2,5</sup> ]-3-decene
	10-methyltricyclo[4,4,0,1 <sup>2,5</sup> ]-3-decene
	1,3-dimethylpentacyclo[6,6,1,1 <sup>3,6</sup> ,0 <sup>2,7</sup> ,0 <sup>9,14</sup> ]-4-hexadecene
	1,6-dimethylpentacyclo[6,6,1,1 <sup>3,6</sup> ,0 <sup>2,7</sup> ,0 <sup>9,14</sup> ]-4-hexadecene

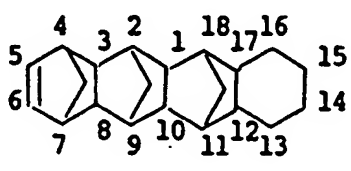
- to be continued -

Table 2 (continued)

Chemical formula	Chemical name
	15,16-dimethylpentacyclo- [6,6,1,1 <sup>3,6</sup> ,0 <sup>2,7</sup> ,0 <sup>9,14</sup> ]- 4-hexadecene
	pentacyclo[6,5,1,1 <sup>3,6</sup> ,0 <sup>2,7</sup> , 0 <sup>9,13</sup> ]-4-pentadecene
	1,3-dimethylpentacyclo- [6,5,1,1 <sup>3,6</sup> ,0 <sup>2,7</sup> ,0 <sup>9,13</sup> ]- 4-pentadecene
	1,6-dimethylpentacyclo- [6,5,1,1 <sup>3,6</sup> ,0 <sup>2,7</sup> ,0 <sup>9,13</sup> ]-4- pentadecene
	14,15-dimethylpentacyclo- [6,5,1,1 <sup>3,6</sup> ,0 <sup>2,7</sup> ,0 <sup>9,13</sup> ]-4- pentadecene
	pentacyclo[6,6,1,1 <sup>3,6</sup> ,0 <sup>2,7</sup> , 0 <sup>9,14</sup> ]-4-hexadecene
	heptacyclo[8,7,1,1 <sup>2,9</sup> ,1 <sup>4,7</sup> , 1 <sup>11,17</sup> ,0,0 <sup>3,8</sup> ,0 <sup>12,16</sup> ]-5- eicosene

- to be continued -

Table 2 (continued)

Chemical formula	Chemical name
	pentacyclo[8,8,1 <sup>2,9,14,7,11,18,0,0,3,8,0,12,17</sup> ]-5-heneicosene

Specific examples of the cyclo-olefins of general formula [III] include cyclopentene, 3-methyl-cyclopentene, 4-methylcyclopentene, 3,4-dimethylcyclopentene, 3,5-dimethylcyclopentene, 3-chlorocyclopentene, cyclohexene, 3-methylcyclohexene, 4-methylcyclohexene, 3,4-dimethylcyclohexene, 3-chlorocyclohexene and cycloheptene.

The cyclo-olefinic random copolymer of this invention contains at least 5 mole%, preferably 15 to 95 mole%, especially preferably 30 to 90 mole%, of recurring units derived from the alpha-olefin component having 3 to 20 carbon atoms, and at least 1 mole%, preferably 5 to 85 mole%, especially preferably 10 to 70 mole%, of recurring units derived from the cyclo-olefin component. When the copolymer of the invention further comprises a cyclic polyene component, the copolymer preferably consists of at least 15 mole% of units derived from the alpha-olefin component, at least 5 mole% of units derived from the cyclic polyene component, and 2 to 80% of units derived from the cyclo-olefin component, and more preferably consists of at least 30 mole% of units derived from the alpha-olefin component (A), at least 10 mole% of units derived from the cyclic polyene component, and at least 5 mole% of units derived from the cyclo-olefin component. The recurring units derived from the C<sub>3</sub>-C<sub>20</sub> alpha-olefin component and the recurring units derived from the cyclo-olefin component are arranged at random to form a substantially linear cyclo-olefinic random copolymer. That the cyclo-olefinic random copolymer of this invention is substantially linear can be ascertained by the fact that the copolymer completely dissolves in decalin at 135 °C.

The intrinsic viscosity [ $\eta$ ], measured in decalin at 135 °C, of the cyclo-olefinic random copolymer of this invention is 0.01 to 10 dl/g, preferably 0.05 to 7 dl/g, especially preferably 0.1 to 5 dl/g.

The molecular-weight distribution ( $\overline{M}_w/\overline{M}_n$ ) of the cyclo-olefinic random copolymer of this invention, measured by gel permeation chromatography (GPC), is usually not more than 4, preferably not more than 3.5, especially preferably not more than 3.

The cyclo-olefinic random copolymer of this invention has a glass transition temperature (T<sub>g</sub>) of 10 to 240 °C, preferably 20 to 200 °C.

The cyclo-olefinic random copolymer of this invention can be produced by polymerizing the alpha-olefin having 3 to 20 carbon atoms with a predetermined amount of the cyclo-olefin and optionally a cyclic polyene component in the presence of a catalyst formed from

(A) a zirconium compound having as a ligand at least two indenyl or substituted indenyl groups or partially hydrogenated groups thereof being bonded via an alkylene group such as an ethylene group, and

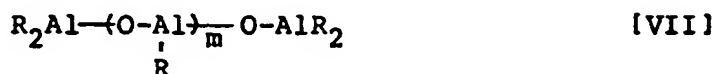
(B) an aluminoxane.

The zirconium compound may have at least two indenyl or substituted indenyl groups or partially hydrogenated groups thereof, preferably two indenyl groups, two substituted indenyl groups, or two partially hydrogenated groups thereof.

Specific examples of the above zirconium compound include

ethylenebis(indenyl)zirconium dichloride,  
ethylenebis(indenyl)zirconium monochloride monohydride,  
ethylenebis(indenyl)ethoxyzirconium chloride,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)ethoxyzirconium chloride,  
ethylenebis(indenyl)dimethylzirconium,  
ethylenebis(indenyl)diethylzirconium,  
ethylenebis(indenyl)diphenylzirconium,  
ethylenebis(indenyl)dibenzylzirconium,  
ethylenebis(indenyl)methylzirconium monobromide,

ethylenebis(indenyl)ethylzirconium monochloride,  
ethylenebis(indenyl)benzylzirconium mono  
chloride,  
ethylenebis(indenyl)methylzirconium monochloride,  
5 ethylenebis(indenyl)zirconium dichloride,  
ethylenebis(indenyl)zirconium dibromide,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-dimethylzirconium,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-ethylzirconium ethoxide,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dichloride,  
10 ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dibromide,  
ethylenebis(4-methyl-1-indenyl)zirconium dichloride,  
ethylenebis(5-methyl-1-indenyl)zirconium dichloride,  
ethylenebis(6-methyl-1-indenyl)zirconium dichloride,  
ethylenebis(7-methyl-1-indenyl)zirconium dichloride,  
15 ethylenebis(5-methoxy-1-indenyl)zirconium dichloride,  
ethylenebis(2,3-dimethyl-1-indenyl)zirconium dichloride,  
ethylenebis(4,7-dimethyl-1-indenyl)zirconium dichloride,  
ethylenebis(4,7-dimethoxy-1-indenyl)zirconium dichloride,  
ethylenebis(indenyl)zirconium dimethoxide,  
20 ethylenebis(indenyl)zirconium diethoxide,  
ethylenebis(indenyl)methoxyzirconium chloride,  
ethylenebis(indenyl)ethoxyzirconium chloride,  
ethylenebis(indenyl)methylzirconium ethoxide,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dimethoxide,  
25 ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium diethoxide,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-methoxyzirconium chloride,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-methylzirconium ethoxide,  
methylenebis(indenyl)zirconium dichloride,  
methylenebis(indenyl)dimethylzirconium,  
30 methylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dichloride,  
propylenebis(indenyl)zirconium dichloride,  
propylenebis(indenyl)dimethylzirconium, and  
propylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dichloride.  
The aluminoxane used as component (b) of the catalyst may be, for example, an organoaluminum  
35 compound represented by the following general formula [VII] or [VIII]



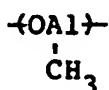
45 wherein R represents a hydrocarbon group such as a methyl, ethyl, n-propyl, isopropyl, n-butyl or isobutyl group, preferably the methyl, ethyl or isobutyl group, especially preferably the methyl group, m is an integer of 2 or more, preferably 5 or more.

The aluminoxane may be produced, for example, by the following method (1) or (2).

50 The aluminoxane of general formula [VII] or [VIII] may be formed of mixed oxyaluminum units



55 having different hydrocarbon groups. In this case, the aluminoxane preferably has at least an oxymethyl aluminum unit



5 in a proportion of at least 30 mole%, preferably at least 50 mole%, especially preferably at least 70 mole%.

(1) A trialkyl aluminum or a mixture of at least two trialkyl aluminums is added to, and reacted with, a suspension of a compound containing water of adsorption or a salt containing water of crystallization, such as magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate  
10 hydrate or cerous chloride hydrate in a hydrocarbon medium.

(2) Water is caused to act directly upon a trialkyl aluminum or a mixture of at least two trialkyl aluminums in a medium such as benzene, toluene, ethyl ether or tetrahydrofuran.

The method (1) is preferred. The aluminoxane may permissibly contain small amounts of organometallic components.

15 The catalyst ingredient (A) or catalyst ingredient (A) and (B) may be used as supported on a carrier. The carrier may be, for example, an inorganic compound such as silica or alumina, or an organic polymeric compound such as polyethylene or polypropylene.

It has been found in accordance with this invention that by copolymerizing the C<sub>3</sub>-C<sub>20</sub> alpha-olefin with the cyclo-olefin in specific proportions using the above catalyst system, a copolymer having properties not  
20 hitherto proposed can be obtained. This copolymerization may be carried out in a liquid phase or in a vapor phase, preferably in the liquid phase. Copolymerization in the liquid phase is usually carried out in a hydrocarbon medium. Examples of the hydrocarbon medium are aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane, alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane, aromatic hydrocarbons  
25 such as benzene, toluene and xylene, and petroleum fractions such as gasoline, kerosene and light oil. The starting olefin may also be used as the hydrocarbon medium. The aromatic hydrocarbons are especially preferred as the hydrocarbon medium.

The temperature in the polymerization reaction in the process of this invention is usually -50 to 230 °C, preferably -30 to 200 °C.

30 The proportion of the zirconium compound used in carrying out the process of this invention in the liquid phase is usually 10<sup>-8</sup> to 10<sup>-2</sup> gram-atom/l, preferably 10<sup>-7</sup> to 10<sup>-3</sup> gram-atom/l, as the concentration of the zirconium atom in the polymerization reaction system. The proportion of the aluminoxane is usually 10<sup>-4</sup> to 10<sup>-1</sup> gram-atom/l, preferably 10<sup>-3</sup> to 5 x 10<sup>-2</sup> gram-atom/l, as the concentration of the aluminum atom in the polymerization reaction system. The ratio of the aluminum atom to the transition  
35 metal atom in the polymerization system is usually from 4 to 10<sup>7</sup>, preferably from 10 to 10<sup>6</sup>. The molecular weight of the copolymer can be adjusted by using hydrogen, and/or adjusting the polymerization temperature.

The present inventors also made investigations for a novel olefinic random copolymer which has excellent transparency, thermal stability, heat aging resistance, chemical resistance, solvent resistance,  
40 dielectric properties and mechanical properties and a narrow molecular weight distribution and a narrow composition distribution, possesses excellent thermal stability even when its cyclo-olefin content is small, and which has a carbon-carbon unsaturated bond capable of reacting with maleic anhydride or the like in its side chain and can be modified easily according to various purposes. These investigations have led to the discovery that a novel olefinic random copolymer can be obtained by copolymerizing an alpha-olefin having  
45 3 to 20 carbon atoms and a cyclic polyene and as required, a cyclo-olefin in the presence of a catalyst formed from a zirconium catalyst and an aluminoxane under specific conditions.

Thus, according to another aspect of this invention there is provided an olefinic random copolymer composed of (A) an olefin component having 3 to 20 carbon atoms and (B) a cyclic polyene component and as required, (C) a cyclo-olefin component,

- 50 (i) said copolymer containing 5 to 99 mole% of recurring units derived from said alpha-olefin component (A) having 3 to 20 carbon atoms and 1 to 95 mole% of recurring units derived from said cyclic polyene component (B) and 0 to 90 mole% of recurring units derived from said cyclo-olefin component (C), and  
(ii) said copolymer having an intrinsic viscosity  $[\eta]$ , measured in decalin at 135 °C, of from 0.01 to 10 dl/g.

The olefinic random copolymer in this embodiment is composed of (A) an alpha-olefin component  
55 having 3 to 20 carbon atoms and (B) a cyclic polyene and as required, (C) a cyclo-olefin component. The cyclo-olefin component (C) is the same cyclo-olefin component of general formula [I], [II] or [III] given hereinabove. As in the aforesaid cyclo-olefinic random copolymer, the cyclo-olefin component forms the structure represented by general formula [IV], [V] or [VI] given hereinabove.

Specific examples of the alpha-olefin used as a starting material in the production of the olefinic random copolymer of this invention may be those given hereinabove.

Specific examples of the cyclic polyene (B) used as a starting material in the production of the olefinic random copolymer of this invention are 1,3-cyclopentadiene, 1,3-cyclohexadiene, 5-ethyl-1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,3-cycloheptadiene, dicyclopentadiene, dicyclohexadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene, 5-isopropylidene-2-norbornene, methylhydroindene, 2,3-diisopropylidene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene, and 2-propenyl-2,5-norbornadiene.

The cyclo-olefinic random copolymer provided by this invention have excellent transparency, thermal stability, heat aging resistance, chemical resistance, solvent resistance, dielectric properties and mechanical properties and a narrow molecular weight distribution and a narrow composition distribution, and possess excellent homogeneity. Because of their excellent properties, they find a wide variety of applications. For example, those having a low molecular weight can be used as synthetic waxes in candles, impregnants for match splints, paper treating agents, sizes, rubber antioxidants, water-proofing agents for corrugated boards, agents for retarding the effect of chemical fertilizers, heat storing agents, binders for ceramics, paper capacitors, electrical insulators for electrical wires and cables, neutron decelerating agents, textile treating aids, water-repellents for building materials, protective agents for paint coatings, lusterants, thixotropy-imparting agents, agents for imparting hardening to the cores of pencils and crayons, carbon ink bases, electrophotographic toners, lubricants and mold releasing agents for molding of synthetic resins, resin coloring agents, hot-melt adhesives and lubricating greases. Those having a high molecular-weight are useful in optical applications as optical lenses, optical discs, optical fibers and windowpanes, electrical applications as water tanks for electrical irons, electric ovens, base plates for liquid crystal display, printed circuit boards, high-frequency circuit boards, and transparent conductive sheets or films, medical applications as injecting syringes, pipettes and animal gages, chemical applications or in other fields as housings of various measuring instruments, camera bodies, films, and helmets.

Those containing not more than about 20 mole% of recurring units from the cyclo-olefin component may be used in fields where their shape memorizing property is utilized, such as vibration controlling materials or tubes. Specifically, they may be used as joints of irregularly-shaped pipes, laminating materials for the inside and outside parts of pipes and rods, clamping pins for optical fiber connectors, plaster bandages, containers, automobile bumpers, various space blocking materials, and vibration control materials (soundproof materials) or medical tubes in the form of laminates with metallic surface materials.

The copolymer of this invention can be easily cured or modified if it contains a carbon-carbon unsaturated bond in its side chain.

In the field of producing cyclo-olefinic copolymers, it has been strongly desired to develop a process which can produce cyclo-olefinic copolymers having a narrow molecular weight distribution efficiently with a high copolymerizing efficiency of cyclo-olefins and excellent polymerization activity. The present inventors recognized that the prior art in the field of producing cyclo-olefinic copolymers was as stated above, and worked on a process which can produce a cyclo-olefinic copolymer having a narrow molecular weight distribution with a high copolymerization efficiency of the cyclo-olefin and excellent polymerization activity. This work has now led to the discovery that the aforesaid object can be achieved by copolymerizing an alpha-olefin and a cyclo-olefin in the presence of a catalyst composed of a compound of a transition metal of Group IVB of the periodic table having a specific coordination compound as a ligand and an aluminoxane.

Thus, according to still another aspect of this invention, there is provided a process for producing a cyclo-olefinic random copolymer, which comprises copolymerizing a  $C_3$  to  $C_{20}$  alpha-olefin and a cyclo-olefin in the presence of a catalyst formed from

(A) a compound of a transition metal of Group IVB of the periodic table having as a ligand a multidentate coordination compound in which at least two conjugated cycloalkadienyl groups or substituted products thereof are bonded via a lower alkylene group, and

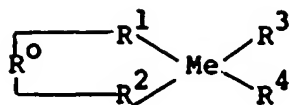
(B) an aluminoxane.

The catalyst used in the process of this invention is formed from (A) a compound of a transition metal of Group IVB of the periodic table and (B) an aluminoxane.

The transition metal compound (A) used as a catalyst ingredient in the process of this invention is a compound of a transition metal of Group IVB of the periodic table which has as a ligand a multidentate coordination compound in which at least two conjugated cycloalkadienyl groups or substituted groups thereof are bonded via a lower alkylene group. The compound of the transition metal of Group IVB of the periodic table are selected from titanium, zirconium and hafnium compounds. Titanium and zirconium are preferred as the transition metal in the catalyst ingredient (A), zirconium being especially preferred.

For example, the Group IVB transition metal compound (A) is represented by the following general formula [IX]

5



[IX]

10 wherein  $R^0$  represents a lower alkylene group, and  $R^1$  and  $R^2$  represent a conjugated cycloalkadienyl group or a substituted group thereof,  $R^3$  and  $R^4$  represent a cycloalkadienyl group, an aryl group, an alkyl group, an aralkyl group, a cycloalkyl group, a halogen atom, a hydrogen atom,  $OR^a$ ,  $SR^b$ ,  $NR^c_2$ , or  $P^d_2$ ,  $R^a$ ,  $R^b$ ,  $R^c$  and  $R^d$  represents a hydrocarbon group such as an alkyl, cycloalkyl, aryl or aralkyl group, or a silyl group, and the  $R^c$  groups and  $R^d$  groups may be linked to form a ring.

15 The lower alkylene group may be, for example, a methylene, ethylene, propylene or butylene group. Examples of the conjugated cycloalkadienyl group include a cyclopentadienyl group, a methylcyclopentadienyl group, an ethylcyclopentadienyl group, a dimethylcyclopentadienyl group, an indenyl group, a tetrahydroindenyl group, and a fluorenyl group. Examples of the alkyl group are methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, 2-ethylhexyl, decyl and oleyl groups. The aryl group may be, for example, a phenyl or tolyl group. The aralkyl groups may be, for example, a benzyl or neophyl group. Examples of the cycloalkyl group include cyclopentyl, cyclohexyl, cyclooctyl, norbornyl and bicyclononyl groups and alkyl-substituted groups thereof. The hydrocarbon group may also include unsaturated aliphatic groups such as vinyl, allyl, propenyl, isopropenyl and 1-butenyl groups, and unsaturated alicyclic groups such as a cyclohexenyl group. The halogen atom may be for example fluorine, chlorine or bromine.

25 The zirconium compounds include, for example, the indenyl-type zirconium compounds exemplified hereinabove, and the following compounds.

Ethylenebis(cyclopentadienyl)zirconium monochloride monohydride,  
ethylenebis(cyclopentadienyl)zirconium dichloride,  
ethylenebis(cyclopentadienyl)methylzirconium monochloride,  
30 ethylenebis(cyclopentadienyl)dimethylzirconium,  
ethylenebis(cyclopentadienyl)diphenylzirconium,  
methylenebis(cyclopentadienyl)zirconium dichloride,  
methylenebis(cyclopentadienyl)dimethylzirconium,  
propylenebis(cyclopentadienyl)zirconium dichloride,  
35 ethylenebis(fluorenyl)zirconium dichloride,  
ethylenebis(fluorenyl)dimethylzirconium,  
ethylenebis(fluorenyl)diphenylzirconium,  
methylenebis(fluorenyl)zirconium dichloride,  
methylenebis(fluorenyl)dimethylzirconium, and  
40 propylenebis(fluorenyl)zirconium dichloride.

Examples of the titanium compounds include  
ethylenebis(indenyl)titanium dichloride,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-titanium dichloride,  
ethylenebis(cyclopentadienyl)titanium dichloride,  
45 methylenebis(cyclopentadienyl)titanium dichloride,  
propylenebis(cyclopentadienyl)titanium dichloride,  
methylenebis(indenyl)titanium dichloride,  
methylenebis(4,5,6,7-tetrahydro-1-indenyl)-titanium dichloride,  
propylenebis(indenyl)titanium dichloride,  
50 ethylenebis(fluorenyl)titanium dichloride, and  
propylenebis(fluorenyl)titanium dichloride.

Examples of the hafnium compounds include the following compounds.

Ethylenebis(cyclopentadienyl)hafnium dichloride,  
methylenebis(cyclopentadienyl)hafnium dichloride,  
55 propylenebis(cyclopentadienyl)hafnium dichloride,  
methylenebis(indenyl)hafnium dichloride,  
methylenebis(4,5,6,7-tetrahydro-1-indenyl)-hafnium dichloride,  
propylenebis(indenyl)hafnium dichloride,



ethylenebis(indenyl)hafnium dichloride, and  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)hafnium dichloride.

The aluminoxane used as the catalyst ingredient (B) may be, for example, the organoaluminum compounds of general formulae [VII] and [VIII] which are exemplified hereinabove.

5 The catalyst ingredient (A) or the catalyst ingredients (A) and (B) may be used as supported on a carrier. The carrier may be, for example, an inorganic compound such as silica or alumina, or an organic polymeric compound such as polyethylene or polypropylene.

Specific examples of C<sub>2</sub>-C<sub>20</sub> alpha-olefins which are used in the polymerization reaction in accordance with the process of this invention include, ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-  
10 octene, 1-decene, 1-octadecene and 1-eicosene.

Specific examples of the cyclo-olefin to be supplied to the polymerization reaction in accordance with the process of this invention include cyclic monoenes, for example monocycloalkenes such as cyclopropene, cyclobutene, cyclopentene, cyclohexene, 3-methylcyclohexene, cycloheptene, cyclooctene, cyclodecene, cyclododecene, tetracyclodecene, octacyclodecene and cycloicosene, bicycloalkenes such as norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, 5-isobutyl-2-norbornene, 5,6-dimethyl-2-  
15 norbornene, and 5,5,6-trimethyl-2-norbornene, tricycloalkenes such as 2,3,3a,7a-tetrahydro-4,7-methano-1H-indene and 3a,5,6,7a-tetrahydro-4,7-methano-1H-indene, tetracycloalkenes such as 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-propyl-1,4,5,8-dimethano-  
20 1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-hexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-stearyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2,3-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-methyl-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-chloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-bromo-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-fluoro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, and 2,3-dichloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene; polycycloalkenes such as hexacyclo[6,6,1,1<sup>3,8</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]heptadecene-4, pentacyclo[8,8,1<sup>2,9</sup>,1<sup>4,7</sup>,1<sup>11,18</sup>,0,0<sup>3,8</sup>,0<sup>12,17</sup>]heneicosene-5, octacyclo[8,8,1<sup>2,9</sup>,1<sup>4,7</sup>,1<sup>11,18</sup>,1<sup>13,16</sup>,0,0<sup>3,8</sup>,0<sup>12,17</sup>]decocene-5; and cyclic polyenes such as dicyclopentadiene, 5-methylene-2-norbornene, 5-ethylidene-2-norbornene, 1,5-cyclooctadiene, 5,8-endomethylenehexahydronaphthalene and alkylidenetetrahydroindenes.

30 In the process of this invention, a mixture of the alpha-olefin and the cyclo-olefin is fed into the polymerization reaction system as a starting material. The content of the alpha-olefin in the mixture is usually 1 to 90 mole%, preferably 2 to 80 mole%, and the content of the cyclo-olefin is usually 10 to 99 mole%, preferably 20 to 98 mole%.

In the process of this invention, the polymerization is usually carried out in a hydrocarbon medium.  
35 Examples of the hydrocarbon medium are aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane, alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane, aromatic hydrocarbons such as benzene, toluene and xylene, and petroleum fractions such as gasoline, kerosene and light oil. The starting olefin may also be used as the hydrocarbon medium. The aromatic hydrocarbons are especially preferred as the hydrocarbon medium.  
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In the process of this invention, a liquid phase polymerization method such as suspension polymerization and solution polymerization and a vapor-phase polymerization method are usually employed. The temperature in the polymerization reaction is usually -50 to 230 °C, preferably -30 to 200 °C.

The proportion of the transition metal compound used in carrying out the process of this invention in the liquid phase is usually 10<sup>-8</sup> to 10<sup>-2</sup> gram-atom/l, preferably 10<sup>-7</sup> to 10<sup>-3</sup> gram-atom/l, as the concentration of the transition metal atom in the polymerization reaction system. The proportion of the aluminoxane is usually 10<sup>-4</sup> to 10<sup>-1</sup> gram-atom/l, preferably 10<sup>3</sup> to 5 x 10<sup>-2</sup> gram-atom/l, as the concentration of the aluminum atom in the polymerization reaction system. The ratio of the aluminum atom to the transition metal atom in the polymerization system is usually from 4 to 10<sup>7</sup>, preferably from 10 to 10<sup>6</sup>. The molecular weight of the copolymer can be adjusted by using hydrogen, and/or adjusting the polymerization temperature.  
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In the process of this invention, a cyclo-olefinic copolymer is obtained by working up the polymerization reaction mixture after the polymerization reaction by conventional methods. The resulting cyclo-olefinic copolymer is usually composed of 20 to 99.9 mole%, preferably 30 to 99.5 mole%, of the alpha-olefin component and 0.1 to 80 mole%, preferably 0.5 to 70 mole%, of the cyclo-olefin component. The intrinsic viscosity [η], measured in decalin at 135 °C, of the cyclo-olefinic copolymer is usually 0.005 to 20 dl/g, preferably 0.01 to 10 dl/g. Its molecular weight distribution measured by gel permeation chromatography is usually not more than 3, preferably not more than 2.5.  
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The process of this invention can produce a cyclo-olefinic random copolymer having a narrow molecular weight distribution with excellent polymerization activity.

The following examples specifically illustrate the cyclo-olefinic random copolymer and the olefinic random copolymer of this invention.

- 5 The properties of the copolymers obtained in the following examples were measured by the following methods.

Copolymer composition (mole%)

- 10 The content of units derived from the cyclo-olefin component in the copolymer was measured by  $^{13}\text{C}$ -NMR (200 megahertz).

Intrinsic viscosity  $[\eta]$

- 15 Measured by an Ubbelohde viscometer at 135 °C.

Molecular weight distribution ( $\bar{M}_w/\bar{M}_n$ )

- 20 Measured by the GPC method.

Glass transition temperature (TG)

Measured by a dynamic mechanical analyzer (DMA) (made by E. I. du Pont de Nemours & Co.).

25 **EXAMPLE 1**

Preparation of ethylenebis(indenyl)zirconium dichloride

- 30 Tetrahydrofuran (60 ml) was fed into a 200 ml fully nitrogen-purged glass flask, and then cooled to -78 °C. Zirconium tetrachloride (4.9 g) was introduced into the flask. The mixture was gradually heated to 60 °C and stirred for 1 hour at this temperature to form a solution. Subsequently, a solution of 21 millimoles of bis(indenyl)ethane lithium salt in 50 ml of tetrahydrofuran was added, and the mixture was stirred at 60 °C for 1 hour. The mixture was further stirred for 12 hours at 25 °C. Under reduced pressure, tetrahydrofuran  
35 was removed to form a solid. The solid was washed with methanol, and dried under reduced pressure to give 2.1g of ethylenebis(indenyl)zirconium dichloride.

Preparation of an aluminoxane

- 40  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  (37 g) and 125 ml of toluene were introduced into a 400 ml fully nitrogen-purged flask, and cooled to 0 °C. Trimethyl aluminum (500 millimoles) diluted with 125 ml of toluene was added dropwise. The mixture was heated to 40 °C, and treated at this temperature for 10 hours. After the reaction, the reaction mixture was filtered. By removing toluene from the filtrate, 13 g of aluminoxane as a white solid was obtained. The aluminoxane had a molecular weight of 930 when it was determined by freezing point  
45 depression in benzene. The  $\bar{m}$  value of the aluminoxane in the catalyst ingredient (B) was 14. For polymerization, the aluminoxane was used as a solution in toluene.

Polymerization

- 50 A 1000 ml fully nitrogen-purged glass autoclave was charged with 500 ml of purified toluene and 15 g of tetracyclododecene, and propylene gas was passed through it at a rate of 60 liters/hr. The flask was maintained at 20 °C for 10 minutes. Subsequently, 5 mg-atom as the aluminum atom of the aluminoxane and  $0.5 \times 10^{-2}$  mg-atom, as the zirconium atom, of ethylenebis(indenyl)zirconium dichloride in toluene were introduced into the autoclave, and the polymerization was started. The polymerization was carried out at 20  
55 °C for 2 hours under atmospheric pressure, and then stopped by adding isopropanol. The polymerization proceeded in a homogeneous solution, and after the 2-hour polymerization, absorption of propylene was observed. The polymer solution was added to a large amount of a mixture of methanol and acetone to precipitate the polymer. The polymer was dried overnight under reduced pressure at 120 °C. After drying,

the amount of the copolymer yielded was 6.1 g. The activity per unit amount of zirconium was 60 g of polymer/mg Zr atom-hr. The resulting copolymer contained 75 mole% of propylene, and had an intrinsic viscosity  $[\eta]$  of 0.09 dl/g, a molecular weight distribution of 1.48, and a glass transition temperature of 78 °C.

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#### EXAMPLES 2-9

Example 1 was repeated except that the copolymerization conditions indicated in Table 3 were employed. The properties of the resulting polymers are also shown in Table 3.

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Table 3

Example	Copolymerization conditions						Properties of the polymer				
	Cyclo-olefin (*3)		$\alpha$ -olefin (*4)		Polymeri- zation tempera- ture (°C)	Polymeri- zation time (hr)	Amount yielded (g)	$\alpha$ -olefin content (mole%)	$[\eta]$ (dl/g)	$\bar{M}_w/\bar{M}_n$	T <sub>g</sub> (°C)
	Name	Concentra- tion in the reactor (g/l)	Name	Concentra- tion in the reactor (g/l)							
1	TD	30	Propylene	60	20	2	6.1	75	0.09	1.48	78
2 (*1)	"	"	"	"	"	4	1.4	70	0.07	1.44	95
3 (*2)	"	"	"	"	"	2	2.2	65	0.07	1.44	123
4	"	"	"	"	0	"	1.1	72	0.20	1.46	89
5	"	"	"	"	50	"	34.4	77	0.11	1.52	67
6	MTD	"	"	"	20	"	5.4	76	0.11	1.45	81
7	NB	"	"	"	"	4	3.6	56	0.15	1.40	110
8	MNB	"	"	"	"	"	3.2	51	0.19	1.44	113
9	"	"	4MP-1	0.5 (l/l)	"	3	0.6	97	0.13	1.30	84

Note: The concentration of Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> was adjusted to 0.1 mmol/l and the concentration of methylaluminoxane, to 10.0 mmol/l.

(\*1): The amount of N<sub>2</sub> fed was adjusted to 180 liters/hr.

(\*2): The amount of N<sub>2</sub> fed was adjusted to 60 liters/hr.

(\*3): TD = tetracyclododecene, MTD = 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8a-octahydronaphthalene, NB = norbornene, MNB = 5-methyl-2-norbornene

(\*4): 4MP-1 = 4-methyl-1-pentene

## EXAMPLE 10

Polymerization

5 A 1000 ml fully nitrogen-purged glass autoclave was charged with 500 ml of purified toluene and 15 g of 4 5-ethylidene-2-norbornene, and propylene gas was passed through it at a rate of 60 liters/hr. 10g/l of Tetracyclododecene was present in the reactor. The flask was maintained at 20 °C for 10 minutes. Subsequently, 5 mg-atom as the aluminum atom of the aluminoxane and  $0.5 \times 10^{-2}$  mg-atom, as the zirconium atom, of ethylenebis(indenyl)zirconium dichloride dissolved in toluene were introduced into the  
10 autoclave, and the polymerization was started. The polymerization was carried out at 20 °C for 4 hours under atmospheric pressure, and then stopped by adding isopropanol. The polymerization proceeded in a homogeneous solution, and after the 4-hour polymerization, absorption of propylene was observed. The polymer solution was added to a large amount of a mixture of methanol and acetone to precipitate the polymer. The polymer was dried overnight under reduced pressure at 120 °C. After drying, the amount of  
15 the copolymer yielded was 2.2 g. The resulting copolymer contained 66 mole% of propylene, and had an intrinsic viscosity  $[\eta]$  0.16 dl/g, and a molecular weight distribution of 1.41.

## EXAMPLES 11-15

20 Example 10 was repeated except that the copolymerization conditions indicated in Table 4 were employed. The properties of the resulting polymers are also shown in Table 4.

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Table 4

Example	Copolymerization conditions							Properties of the polymer					
	Propylene		Cyclic polyene (*1)		Cyclo-olefin (*2)		Polymeri- zation tempera- ture (°C)	Polymeri- zation time (hr)	Amount yielded (g)	Cyclic polyene content (mole%)	cyclo- olefin content (mole%)	$[\eta]$ (dl/g)	$\bar{M}_w/\bar{M}_n$
	Concentra- tion in the reactor (g/hr)	Name	Concentra- tion in the reactor (g/l)	Name	Concentra- tion in the reactor (g/l)								
10	60	ENB	30	TD	10	20	4	2.0	31	8	0.11	1.48	
11	"	"	"	"	30	"	"	1.7	25	17	0.09	1.49	
12	"	"	"	NB	10	"	"	2.1	29	11	0.14	1.45	
13	"	VNB	"	TD	10	"	"	1.7	28	7	0.12	1.46	
14	"	"	"	"	30	"	"	1.4	21	16	0.10	1.47	
15	"	"	"	NB	10	"	"	1.8	28	13	0.13	1.43	

Note: The concentration of Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> was adjusted to 0.1 mm/l and the concentration of methylaluminoxane, to 10.0 mm/l.

(\*1): ENB = ethylidene-2-norbornene, VNB = 5-vinyl-2-norbornene

(\*2): TD = tetracyclododecene, NB = norbornene

# EXAMPLE 16

A 1000 ml fully nitrogen-purged glass autoclave was charged with 500 ml of purified toluene and 15 g of tetracyclododecene, and propylene gas was passed through it at a rate of 60 liters/hr. The flask was

maintained at 20 °C for 10 minutes. Subsequently, 5 mg-atom as the aluminum atom of the aluminoxane and  $0.5 \times 10^{-2}$  mg-atom, as the zirconium atom, of ethylenebis(indenyl)zirconium dichloride in toluene were introduced into the autoclave, and the polymerization was started. The polymerization was carried out at 20 °C for 2 hours under atmospheric pressure, and then stopped by adding isopropanol. The polymerization  
 5 proceeded in a homogeneous solution, and after the 2-hour polymerization, absorption of propylene was observed. The polymer solution was added to a large amount of a mixture of methanol and acetone to precipitate the polymer. The polymer was dried overnight under reduced pressure at 120 °C. After drying, the amount of the copolymer yielded was 6.1 g. The activity per unit amount of zirconium was 60 g of polymer/mg Zr atom-hr. The resulting copolymer contained 75 mole% of propylene, and had an intrinsic  
 10 viscosity  $[\eta]$  of 0.09 dl/g and a molecular weight distribution of 1.48.

#### EXAMPLE 17

Example 16 was repeated except that the amount of purified toluene was changed to 250 ml, 15 g of 5-methyl-1-pentene was used instead of the tetracyclododecene and 250 ml of 4-methyl-1-pentene was used instead of propylene, and the polymerization was carried out at 20 °C for 3 hours. There was obtained 0.6 g of a copolymer having a 4-methyl-1-pentene content of 97 mole%, an intrinsic viscosity  $[\eta]$  of 0.13 dl/g and a molecular weight distribution of 1.30.

#### 20 Claims

1. A cyclo-olefinic random copolymer consisting of units derived from (A) an alpha-olefin component having 3 to 20 carbon atoms, (B) an optional cyclic polyene component, and (C) a cyclo-olefin component,  
 25 (i) said copolymer containing at least 5 mole% of recurring units derived from said alpha-olefin component and at least 1 mole% of recurring units derived from said cyclo-olefin component, subject to the proviso that when the copolymer is derived also from the cyclic polyene component it contains at least 1 mole% of recurring units derived from said cyclic polyene component and from 2 to 80 mole% of recurring units from said cyclo-olefin component, and  
 30 (ii) said copolymer having an intrinsic viscosity  $[\eta]$ , measured in decalin 135 °C, of from 0.01 to 10 dl/g.
2. A copolymer according to claim 1 which consists of 15 to 95 mole% of units derived from said alpha-olefin component and 85 to 5 mole% of units derived from said cyclo-olefin component.
- 35 3. A copolymer according to claim 1 which consists of 30 to 90 mole% of units derived from said alpha-olefin component and 70 to 10 mole% of units derived from said cyclo-olefin component.
4. A copolymer according to claim 1, 2 or 3 which consists of units derived from (A) propylene or 4-methyl-1-pentene, and (B) tetracyclododecene, 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, norbornene or 5-methyl-2-norbornene.
- 40 5. A copolymer according to claim 1 which consists of at least 15 mole% of units derived from the alpha-olefin component, at least 5 mole% of units derived from the cyclic polyene component, and 2 to 80 mole% of units derived from the cyclo-olefin component.
- 45 6. A copolymer according to claim 5 which consists of at least 30 mole% of units derived from the alpha-olefin component (A), at least 10 mole% of units derived from the cyclic polyene component, and at least 5 mole% of units derived from the cyclo-olefin component.
- 50 7. A copolymer according to claim 1, 5 or 6 wherein the alpha-olefin component (A) is propylene, the cyclic polyene component (B) is 5-ethylidene-2-norbornene or 5-vinyl-2-norbornene, and the cyclo-olefin component (C) is tetracyclododecene or norbornene.
- 55 8. A copolymer according to any one of the preceding claims which has an intrinsic viscosity  $[\eta]$ , measured in decalin at 135 °C, of 0.5 to 7 dl/g.

9. A copolymer according to claim 8 which has an intrinsic viscosity  $[\eta]$ , measured in decalin at 135 °C, of 0.5 to 5 dl/g.
10. A process for producing a cyclo-olefinic random copolymer as claimed in any one of the preceding claims, which comprises copolymerizing the alpha-olefin, the cyclo-olefin and optionally also the cyclic polyene in the presence of a catalyst formed from
- (A) a compound of a transition metal of Group IVB of the periodic table having as a ligand a multi-dentate coordination compound in which at least two conjugated cycloalkadienyl groups or substituted products thereof are bonded via a lower alkylene group, and
- (B) an aluminoxane, subject to the proviso that when the cyclic polyene is present the transition metal compound (A) is a zirconium compound containing as ligand at least two indenyl groups or substituted indenyl groups or partially hydrogenated groups thereof which are bonded via an alkylene group.
11. A process according to claim 10 wherein when only the alpha-olefin and the cyclo-olefin are copolymerized the transition metal compound is a zirconium compound containing as a ligand at least two indenyl groups or substituted indenyl groups or partially hydrogenated groups thereof which are bonded via an alkylene group.
12. A process according to claims 10 or 11 wherein the transition metal compound is ethylenebis(indenyl)-zirconium dichloride.
13. A process according to claim 10, 11 or 12 wherein the aluminoxane is represented by the general formula
- $$\begin{array}{c} \text{R}_2\text{Al}-\text{O}-\underset{\text{R}}{\underset{|}{\text{Al}}}-\text{O}-\text{AlR}_2 \\ \text{m} \end{array} \quad \text{[VII]}$$
- $$\begin{array}{c} \boxed{\text{Al(R)-O}} \\ \text{m+2} \end{array} \quad \text{[VIII]}$$
- wherein R represents a hydrocarbon group, and m represents an integer of at least 2.
14. A process according to claim 13 wherein R is a methyl, ethyl or isobutyl group, and m is an integer of at least 5.
15. A process according to claim 13 wherein R is a methyl group and m is an integer of 5 to 50.
16. A process according to any one of claims 10 to 15 wherein only the alpha-olefin and the cyclo-olefin are polymerized and the alpha-olefin is selected from propylene and 4-methyl-1-pentene, and the cyclo-olefin is selected from tetracyclododecene, 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2,3-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8, 8a-octahydronaphthalene, 5-methyl-2-norbornene, norbornene and 5-ethylidene-2-norbornene.

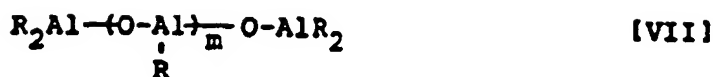
#### Patentansprüche

1. Statistisches Cycloolefin-Copolymer, enthaltend Einheiten, abgeleitet von (A) einer  $\alpha$ -Olefinkomponente mit 3 bis 20 Kohlenstoffatomen, (B) einer gegebenenfalls vorhandenen cyclischen Polylenkomponente und (C) einer Cycloolefinkomponente, wobei
- (i) das Copolymer mindestens 5 mol-% wiederkehrende Einheiten enthält, abgeleitet von der  $\alpha$ -Olefinkomponente, und mindestens 1 mol-% wiederkehrende Einheiten, abgeleitet von der Cycloolefinkomponente, mit der Maßgabe, daß, wenn das Copolymer auch abgeleitet ist von der cyclischen Polylenkomponente, es mindestens 1 mol-% wiederkehrende Einheiten enthält, abgeleitet von der cyclischen Polylenkomponente, und 2 bis 80 mol-% wiederkehrende Einheiten von der Cycloolefinkomponente, und



(ii) das Copolymer eine Grenzviskosität  $[\eta]$ , gemessen in Decalin bei 135 °C, von 0,01 bis 10 dl/g aufweist.

2. Copolymer nach Anspruch 1, bestehend aus 15 bis 95 mol-% Einheiten, abgeleitet von der  $\alpha$ -Olefinkomponente, und 85 bis 5 mol-% Einheiten, abgeleitet von der Cycloolefinkomponente.
3. Copolymer nach Anspruch 1, bestehend aus 30 bis 90 mol-% Einheiten, abgeleitet von der  $\alpha$ -Olefinkomponente, und 70 bis 10 mol-% Einheiten, abgeleitet von der Cycloolefinkomponente.
4. Copolymer nach Anspruch 1, 2 oder 3, bestehend aus Einheiten, abgeleitet von (A) Propylen oder 4-Methyl-1-penten, und (B) Tetracyclododecen, 2-Methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin, Norbornen oder 5-Methyl-2-norbornen.
5. Copolymer nach Anspruch 1, bestehend aus mindestens 15 mol-% Einheiten, abgeleitet von der  $\alpha$ -Olefinkomponente, mindestens 5 mol-% Einheiten, abgeleitet von der cyclischen Polyenkomponente, und 2 bis 80 mol-% Einheiten, abgeleitet von der Cycloolefinkomponente.
6. Copolymer nach Anspruch 5, bestehend aus mindestens 30 mol-% Einheiten, abgeleitet von der  $\alpha$ -Olefinkomponente (A), mindestens 10 mol-% Einheiten, abgeleitet von der cyclischen Polyenkomponente, und mindestens 5 mol-% Einheiten, abgeleitet von der Cycloolefinkomponente.
7. Copolymer nach Anspruch 1, 5 oder 6, wobei die  $\alpha$ -Olefinkomponente (A) Propylen ist, die cyclische Polyenkomponente (B) 5-Ethyliden-2-norbornen oder 5-Vinyl-2-norbornen ist und die Cycloolefinkomponente (C) Tetracyclododecen oder Norbornen ist.
8. Copolymer nach einem der vorangehenden Ansprüche, mit einer Grenzviskosität  $[\eta]$ , gemessen in Decalin bei 135 °C, von 0,5 bis 7 dl/g.
9. Copolymer nach Anspruch 8, das eine Grenzviskosität  $[\eta]$ , gemessen in Decalin bei 135 °C, von 0,5 bis 5 dl/g aufweist.
10. Verfahren zur Herstellung eines statistischen Cycloolefin-Copolymers nach einem der vorangehenden Ansprüche, umfassend das Copolymerisieren des  $\alpha$ -Olefins, des Cycloolefins und gegebenenfalls auch des cyclischen Polyens in Gegenwart eines Katalysators, gebildet aus
  - (A) einer Verbindung eines Übergangsmetalls der Gruppe IVB des Periodensystems, die als Liganden eine mehrzahnige Koordinationsverbindung besitzt, bei der mindestens zwei konjugierte Cycloalkadienylgruppen oder substituierte Produkte davon über eine niedere Alkylengruppe gebunden sind, und
  - (B) einem Aluminoxan, mit der Maßgabe, daß, wenn das cyclische Polyen vorhanden ist, die Übergangsmetallverbindung (A) eine Zirkoniumverbindung ist, enthaltend als Liganden mindestens zwei Indenylgruppen oder substituierte Indenylgruppen oder partiell hydrierte Gruppen davon, die über eine Alkylengruppe gebunden sind.
11. Verfahren nach Anspruch 10, wobei, wenn nur das  $\alpha$ -Olefin und das Cycloolefin copolymerisiert werden, die Übergangsmetallverbindung eine Zirkoniumverbindung ist, enthaltend als Liganden mindestens zwei Indenylgruppen oder substituierte Indenylgruppen oder partiell hydrierte Gruppen davon, die über eine Alkylengruppe gebunden sind.
12. Verfahren nach Anspruch 10 oder 11, wobei die Übergangsmetallverbindung Ethylen-bis-(indenyl)-zirkonium-dichlorid ist.
13. Verfahren nach Anspruch 10, 11 oder 12, wobei das Aluminoxan angegeben ist durch die allgemeine Formel



10      wobei R eine Kohlenwasserstoffgruppe darstellt und m eine ganze Zahl von mindestens 2 ist.

14. Verfahren nach Anspruch 13, wobei R eine Methyl-, Ethyl- oder Isobutylgruppe ist und m eine ganze Zahl von mindestens 5.

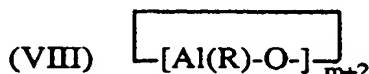
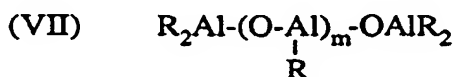
15    15. Verfahren nach Anspruch 13, wobei R eine Methylgruppe und m eine ganze Zahl von 5 bis 50 ist.

16. Verfahren nach einem der Ansprüche 10 bis 15, wobei nur das  $\alpha$ -Olefin und das Cycloolefin copolymerisiert werden und das  $\alpha$ -Olefin ausgewählt ist aus Propylen und 4-Methyl-1-penten und das Cycloolefin ausgewählt ist aus Tetracyclododecen, 2-Methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronephthalin, 2,3-Dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronephthalin, 5-Methyl-2-norbornen, Norbornen und 5-Ethyliden-2-norbornen.

#### Revendications

- 25    1. Copolymère statistique cyclo-oléfinique, constitué d'unités dérivées
  - (A) d'un composant  $\alpha$ -oléfinique comportant de 3 à 20 atomes de carbone,
  - (B) d'un composant polyénique cyclique facultatif, et
  - (C) d'un composant cyclo-oléfinique,
  - 30      (i) ledit copolymère contenant au moins 5 % en moles d'unités répétitives dérivées dudit composant  $\alpha$ -oléfinique et au moins 1 % en moles d'unités répétitives dérivées dudit composant cyclo-oléfinique, à condition que, lorsque le copolymère contient également le composant polyénique cyclique, il contient au moins 1 % en moles d'unités répétitives dudit composant polyénique cyclique et de 2 à 80 % en moles d'unités répétitives dudit composant cyclo-oléfinique, et
  - 35      (ii) ledit copolymère ayant une viscosité intrinsèque  $[\eta]$ , mesurée dans la Décaline® à 135 °C, comprise entre 0,01 et 10 dl/g.
2. Copolymère conforme à la revendication 1 constitué de 15 à 95 % en moles d'unités dérivées dudit composant  $\alpha$ -oléfinique et de 85 % à 5 % en moles d'unités dérivées dudit composant cyclo-oléfinique.
3. Copolymère conforme à la revendication 1 constitué de 30 à 90 % en moles d'unités dérivées dudit composant  $\alpha$ -oléfinique et de 70 à 10 % en moles d'unités dérivées dudit composant cyclo-oléfinique.
- 45    4. Copolymère conforme à la revendication 1, 2 ou 3 constitué d'unités dérivées de
  - (A) propylène ou 4-méthyl-1-pentène, et
  - (B) tétracyclodécène, 2-méthyl-1,4,5,8-diméthano-1,2,3,4,4a,5,8, 8a-octahydronephthalène, norbornène ou 5-méthyl-2-norbornène.
- 50    5. Copolymère conforme à la revendication 1 constitué d'au moins 15 % en moles d'unités dérivées du composant  $\alpha$ -oléfinique, d'au moins 5 % en moles d'unités dérivées du composant polyénique cyclique et de 2 à 80 % en moles d'unités dérivées du composant cyclo-oléfinique.
- 55    6. Copolymère conforme à la revendication 5, constitué d'au moins 30 % en moles d'unités dérivées du composant  $\alpha$ -oléfinique (A), d'au moins 10 % en moles d'unités dérivées du composant polyénique cyclique et d'au moins 5 % en moles d'unités dérivées du composant cyclo-oléfinique.

7. Copolymère conforme à la revendication 1, 5 ou 6 dans lequel le composant  $\alpha$ -oléfinique (A) est le propylène, le composant polyénique cyclique (B) est le 5-éthylidène-2-norbornène ou le 5-vinyl-2-norbornène, et le composant cyclo-oléfinique (C) est le tétracyclodécène ou le norbornène.
8. Copolymère conforme à une quelconque des revendications précédentes ayant une viscosité intrinsèque  $[\eta]$ , mesurée dans la Décaline® à 135 °C comprise entre 0,5 et 7 dl/g.
9. Copolymère conforme à la revendication 8 ayant une viscosité intrinsèque  $[\eta]$ , mesurée dans la Décaline® à 135 °C comprise entre 0,5 et 5 dl/g.
10. Procédé pour la préparation d'un copolymère statistique cyclo-oléfinique conforme à une quelconque des revendications précédentes, consistant à copolymériser l' $\alpha$ -oléfine, la cyclo-oléfine, et facultativement le polyène cyclique en présence d'un catalyseur formé à partir
- (a) d'un composé d'un métal de transition du groupe IVB du tableau périodique des éléments, ayant comme ligand un composé de coordination multidenté dans lequel au moins deux groupes cycloalcadiényle conjugués ou des dérivés substitués de ceux-ci sont liés par un groupe alkylène inférieur et
- (b) un aluminoxane, à condition que, lorsque le polyène cyclique est présent, le composé du métal de transition (A) est un composé de zirconium contenant comme ligand au moins deux groupes indényle, indényle substitué ou indényle partiellement hydrogéné, liés par un groupe alkylène.
11. Procédé conforme à la revendication 10, dans lequel, lorsque seules l' $\alpha$ -oléfine et la cyclo-oléfine sont copolymérisées, le composé de métal de transition est un composé de zirconium contenant, comme ligand, au moins deux groupes indényle, indényle substitué ou indényle partiellement hydrogéné, liés par un groupe alkylène.
12. Procédé conforme à la revendication 10 ou 11 dans lequel le composé de métal de transition est le dichlorure d'éthylène-bis-(indényle)zirconium.
13. Procédé conforme à la revendication 10, 11 ou 12 dans lequel l'aluminoxane est représenté par la formule générale



dans lesquelles R représente un groupe hydrocarboné et m représente un nombre entier au moins égal à 2.

14. Procédé conforme à la revendication 13 dans lequel R représente un groupe méthyle, éthyle ou isobutyle et m est un nombre entier au moins égal à 5.
15. Procédé conforme à la revendication 13 dans lequel R représente un groupe méthyle et m est un nombre entier compris entre 5 et 50.
16. Procédé conforme à une quelconque des revendications 10 à 15 dans lequel seules l' $\alpha$ -oléfine et la cyclo-oléfine sont copolymérisées et l' $\alpha$ -oléfine est choisie parmi le propylène et le 4-méthyl-1-pentène, et la cyclo-oléfine est choisie parmi le tétracyclodécène, le 2-méthyl-1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène, le 2,3-diméthyl-1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène, le 5-méthyl-2-norbornène, le norbornène et le 5-éthylidène-2-norbornène.